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by

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Light Stability of Polyurethane Coatings

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Abstract

The photodegradation of methylene 4,4'-diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) based polyurethanes is reported to be dependent on backbone chain flexibility and matrix crystallinity. Both absorbance changes and gel formation decrease as the stiffness and crystalline content of powders and films increase. Stabilizers are only marginally effective in reducing the extent of degradation of the polyurethane films.
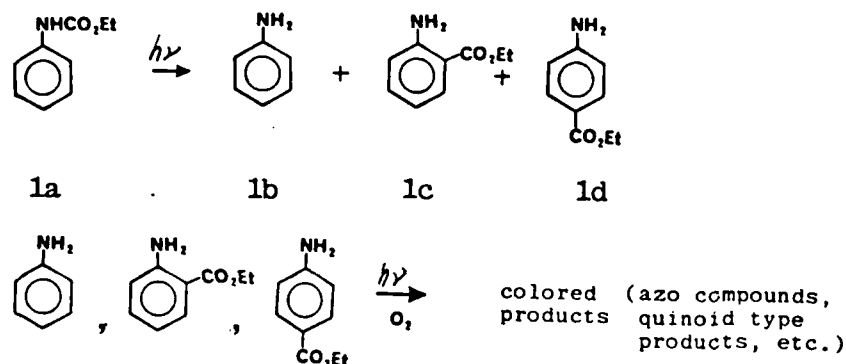
Introduction

Since the discovery of diisocyanate polymerization reactions by Otto Bayer in the late 1930's, the use of polyurethanes in diverse applications ranging from rigid foams to coatings and adhesives has experienced a rapid rate of growth with excellent prospects for continued progress in the future. Polyurethanes which are employed in commercial applications today are based on both aliphatic and aromatic diisocyanates. While there is a distinct economic advantage in the use of the aromatic diisocyanates, their use in applications where the resultant polyurethanes are exposed to UV radiation is limited due to a rapid deterioration in physical and mechanical properties (tensile strength, impact strength, extensibility, etc.) accompanied by severe discoloration (1-11). Thus, when consideration is given to choosing diisocyanates for use in protective coatings applications, aliphatics are attractive due to their UV stability and not their cost.

Recognizing the obvious advantage of being in a position to employ aromatic instead of aliphatic diisocyanates, studies centered on understanding the mechanism of the UV degradation of aromatic diisocyanate based polyurethanes have been conducted over the past two decades with varying results. In the 1960's and early 1970's, Schollenberger and coworkers (5-7) and Nevskii, Tarakanov, and coworkers (8-12) conducted extensive studies on the photodegradation of polyurethanes based on aromatic diisocyanates such as methylene 4,4'-diphenyl diisocyanate (MDI) and toluene diisocyanate (represents a mixture of the 2,4-toluene diisocyanate (2,4-TDI) and 2,6-toluene diisocyanate (2,6-TDI) isomers). Based on changes in physical properties, UV spectra, IR spectra, and chemical reactivity, both groups postulated that formation of quinone-imide type chromophores are primarily responsible for the discoloration and mechanical property losses of aromatic diisocyanate based polyurethanes upon photolysis (Scheme I).
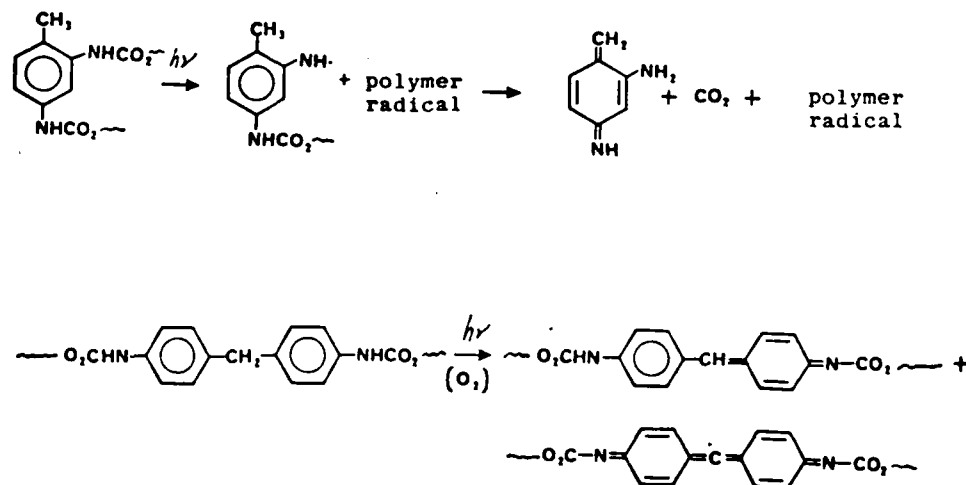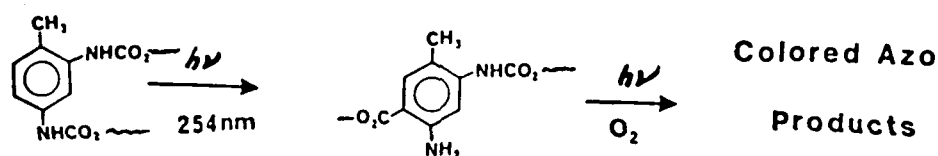

Scheme I

In work on the photolysis of model aryl carbamates (13-23) such as ethyl N-phenylcarbamate, it was found that photo-Fries rearrangement products are generated in the initial photolysis step (Step 1 - Scheme II). Beachell and Chang (13) clearly demonstrated that discoloration was then produced by secondary photolysis (Step 2 - Scheme II) of the aryl amines generated in the first photolysis step.

$$
\text{1a} \xrightarrow{h\nu} \text{1b} + \text{1c} + \text{1d}
$$

1a . 1b 1c 1d

$$
\text{(aryl amines)} \xrightarrow[O_2]{h\nu} \text{colored products (azo compounds, quinoid type products, etc.)}
$$

Scheme II

They proposed that photodegradation of 2,4-TDI based polyurethanes proceeds by a mechanism similar to that in Scheme II to give a series of colored azo compounds (Scheme III).

$$
\xrightarrow[254\,nm]{h\nu} \quad \xrightarrow[O_2]{h\nu} \text{Colored Azo Products}
$$

Scheme III

Despite the apparent difference between Schollenberger's (Scheme I) and Beachell's (Scheme III) proposed mechanism for photodegradation of 2,4-TDI based polyurethanes, both postulated an initial N-C bond cleavage as the primary photochemical reaction of

the aryl carbamate. The N-C bond cleavage was confirmed by Osawa et. al. (Scheme IV, ref. 24) who used ESR to detect both an N-C and a C-O bond cleavage upon photolysis of an MDI based polyurethane. In both cases a substituted anilinyl radical is ultimately formed.
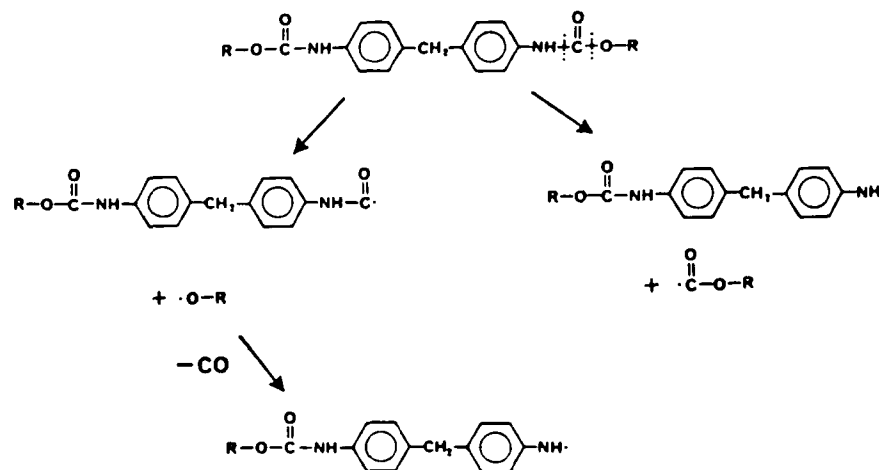
Scheme IV

In an attempt to consolidate the results of Nevskii and Schollenberger (Scheme I) with Beachell (Schemes II and III), Gardette and Lemaire (25-27) studied the effect of excitation wavelength on the photolysis of MDI based polyurethanes. By comparison of IR and UV spectra for polyurethane films as a function of photolysis time, they suggested that photodegradation of MDI based polyurethanes proceeds by two processes (Scheme V). One yields the quinone-imide type product proposed by Nevskii (8-12) and Schollenberger (5-7) and the other affords the photo-Fries rearrangement product(s) postulated by Schwetlick (16-18) and Beachell and Chang (15).
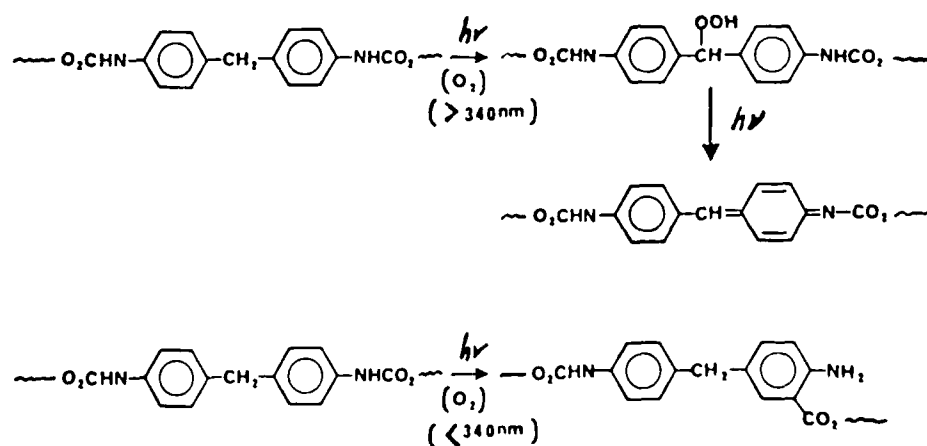
Scheme V

Gardette and Lemaire concluded that photolysis with light of wavelength below 330 nm gives primarily a photo-Fries rearrangement type product (along with a cage separated aryl amine product) while photolysis above 340 nm causes photo-oxidation resulting in the formation of labile hydroperoxides. The hydroperoxides then undergo, according to Gardette and Lemaire (29), a photolytic decomposition to the quinone-imide and/or other colored products. It should be noted that aside from UV spectral data no new evidence for photo-Fries and/or quinone-imide products was given by Gardette and Lemaire.

In reviewing the previous photolysis studies of aromatic diisocyanate based polyurethanes, two obvious and quite important points dealing with the degradation mechanism become apparent. First, is it possible to more conclusively identify products formed from a photo-Fries type rearrangement process in the actual polyurethane films by extending the results from model compound studies in solution? Second, what effect, if any, does the physical state (amorphous, crystalline) and chain flexibility of the polyurethane have on the photodegradation process? These are questions which are directly addressed in the current paper. Drawing on representative results from our studies of the photolysis of aromatic diisocyanate based polyurethanes, fluorescence spectroscopy is used to identify the ortho photo-Fries rearrangement products obtained upon photolysis of MDI and 2,4-TDI based polyurethanes. Using a combination of fluorescence spectroscopy, absorption spectroscopy, and percent crosslinked gel formation, the effect of polymer chain flexibility and polymer crystallinity on the photodegradation of polyurethanes is explored.

Experimental

Materials. Methylene 4,4'-diphenyldiisocyanate (MDI-Mobay) was recrystallized before use. 2,4-toluene diisocyanate (2,4-TDI) (99.5% Mobay) was purified by distillation. Dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) (Baker) were distilled and dried. Diols (Aldrich) used in polyurethane preparation were either distilled or recrystallized from 1,2-dichloroethane. The preparation of the model aryl carbamate and resulting products has been reported earlier (17). Polyurethanes based on aliphatic diols and MDI (or 2,4-TDI) were prepared by a typical solution polymerization (28) with no added catalyst. Polyurethanes based on oligo oxyethylenes and MDI were prepared as above with 1.5% dibutyltin dilaurate. Polyurethane elastomers were prepared by a two step method. First 0.01 moles of MDI was dissolved in 15 ml DMSO and 0.005 moles of poly(ethylene glycol) solution was then added dropwise to the MDI solution and heated for 2 hr at 50°C. To the resultant solution, 0.005 moles of butane diol in a 10 ml DMSO solution was added dropwise and the solution was heated for 12 hr at 80°C. (In all cases of polyurethane synthesis complete cure was indicated by loss of isocyanate absorbance in the IR).

The subsitited benzotriazole (Tinuvin 328) light screener and, the hindered amine light stabilizer [Tinuvin 292 — bis(1,2,2,6,6-pentamethyl-4-piperidinyl)sebacate] were kindly supplied by the Ciba-Geigy Corporation.

Procedures/Instrumentation

Photolysis of the DMF solution of ethyl N-phenylcarbamate was conducted in a Rayonet Reactor with 300 nm lamps. Photolysis of the 2,4-TDI—dodecanediol polyurethane powder and the MDI polyurethanes for fluorescence analysis were conducted using a Xenon lamp/monochromator combination with 10 nm slits. Photolysis of 2,4-TDI—dodecanediol polyurethane films were accomplished using a 100 Watt medium pressure mercury lamp with merry-go-round from Canrad Hanovia. The MDI—dodecanediol film used for gel formation was photolyzed in a Rayonet Reactor with 300 nm lamps.

All films were cast from DMF solutions. The 2,4-TDI—aliphatic diol polyurethane films were heated for 1 hr at 70°C in a vacuum oven before photolysis. The MDI—dodecanediol polyurethane films were heated at 160°C for 30 minutes (semi-crystalline film). In the case of the quenched film this process was followed by heating above the melting point followed by a rapid quenching at room temperature (essentially amorphous film obtained). The elastomer polyurethane films were heated in a vacuum oven at 70°C for 1 hr prior to photolysis. All films were subjected to DSC and/or X-ray analysis where appropriate to obtain melting point, glass transition, and crystallinity data (the analysis of the polymers obtained will be published in a full paper).

Results and Discussion

Photolysis of Model Aryl Carbamate

In order to provide basic identification of product(s) formed from the photolysis of aromatic diisocyanate based polyurethanes, our first step is to conduct a detailed fluorescence analysis of the photolysis of a model aryl carbamate whose solution photochemistry is documented (13-18). It is then a simple step to apply the same fluorescence analysis technique to investigate the photolysis of solid (powder or films) polyurethanes based on 2,4-TDI and MDI. Choosing ethyl N-phenylcarbamate as the model, the fluorescence maxima of the parent carbamate (1a), and the three major resulting photoproducts (1b-1d) are given in Table I. Particularly noteworthy is the highly red-shifted fluorescence maximum (above 400 nm) of the ortho photo-Fries product (1c). This red-shift is indicative of a stabilized excited state due to an ortho substituted amino group. Figure 1 shows results for the photolysis of 1a (2.5 X 10^{-4}M in DMF) in a Rayonet Reactor (300 nm Lamps) for 5 hours. As expected, loss in fluorescence from the parent aryl carbamate is accompanied by the appearance of emission from photoproducts 1b, 1c, and 1d as indicated in Figure 1. Particularly distinctive is the red-shifted emission from the ortho photo-Fries product 1c.

Having developed a convenient fluorescence technique for evaluation of the photolysis of aryl carbamates in solution, we turn to the more interesting, and perhaps more challenging, investigation of the photodegradation of films/powders of polyurethanes based on 2,4-TDI and MDI. Our first goal is to identify the formation of photo-Fries rearrangement products in the film/powder state of aromatic diisocyanate based polyurethanes. Second, since films and powders of aromatic diisocyanate based polyurethanes may exist in a wide variety of forms, depending on the nature of the aliphatic (non-carbamate) and aromatic (carbamate) portions of the polyurethanes, consideration of the structural (chain mobility) and morphological (crystallinity) effects on the photodegradation process are of paramount importance. Thus, we have measured fluorescence spectral changes in order to elucidate the mechanism of photodegradation of aromatic diisocyante based polyurethanes in the solid state (films and powders). Results for the 2,4-TDI and MDI based polyurethane are covered individually in the next few paragraphs.

Photolysis of 2,4-TDI Based Polyurethanes

Essentially all polyurethanes based on 2,4-TDI are amorphous regardless of the nature of the aliphatic portion of the polymer. Figure 2 shows the fluorescence spectrum of a polyurethane made from 2,4-TDI and dodecanediol before and after photolysis (2 hours, 280 nm, Xenon lamp). The fluorescence spectrum of the photolyzed sample clearly indicates the formation of an ortho photo-Fries product with emission maximum at 420 ± 10 nm. The presence of a para photo-Fries or aryl amine cleavage product could not be either confirmed or repudiated with sufficient confidence. This appears to be a general phenomenon associated with our analysis of photolyzed aromatic diisocyanate based polyurethane films/powders.

In addition to fluorescence analysis, the photolysis of polyurethanes can also be followed both by absorbance increases (typically at 400 nm) and crosslinked insoluble gel formation. Figures 3 and 4 illustrate the increases in 400 nm absorbance and gel formation for photolysis of a 2,4-TDI--dodecanediol and a 2,4-TDI--decanediol polyurethane film, respectively (100 Watt, medium pressure mercury lamp).

Although the exact nature of the absorbance at 400 nm and the gel formation is not conclusively established, both are accepted measures of polyurethane degradation and can be used to probe the effect of polymer chain flexibility on the degradation process. Thus, a series of polyurethanes based on 2,4-TDI and short chain aliphatic diols, i.e., ethanediol (n=2), butanediol (n=4), hexanediol (n=6), octanediol (n=8), decanediol (n=10), and dodecanediol (n=12) have been synthesized where n corresponds to the number of methylene segments in the aliphatic diol. These polyurethanes are characterized (Tg analysis) by an increasing flexibility with increasing length of the aliphatic chain. Interestingly, as shown in Figures 5 and 6, both the absorption at 400 nm and the gel content

increases with increasing length of the aliphatic portion of the polyurethane. In general, then, it can be concluded that the polyurethane chain flexibility must be taken into account in the overall photodegradation process.

Before concluding the discussion on 2,4-TDI based polyurethanes, the effect of stabilizers (both UV absorbing and hindered amine type) on the photodegradation process is briefly considered. Choosing the 2,4-TDI--dodecanediol polymer, the effect of two stabilizer systems on the absorbance increase at 400 nm (indicative of yellowing in the polymer) is shown in Figure 7. The stabilizers employed have the structures shown below.
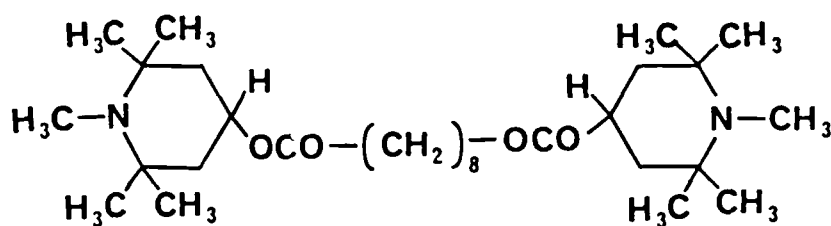
HALS
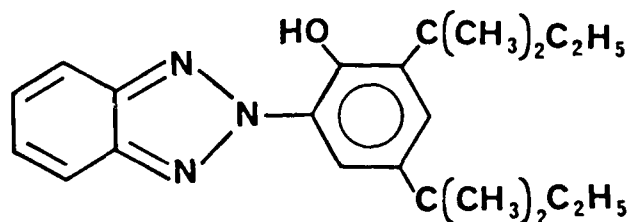
Substituted Benzotriazole

Although the substituted benzotriazole, which stabilizes by competitive absorption, is the most efficient of the two systems at

the concentrations employed, it should be pointed out that the hindered amine light stabilizer (HALS) is still useful as a stabilizing system. (Note that no attempt was made to optimize the concentration of the stabilizers.)

Photolysis of MDI Based Polyurethanes

Polyurethanes based on MDI and oligo oxyethylenes may exhibit either amorphous or semi-crystalline structures in the solid state depending on the number of oxyethylene linkages in the ether portion of the polyurethane. Photolysis at 280 nm (Xenon lamp) of the semi-crystalline (DSC, X-ray analysis) powder based on MDI and diethylene glycol results in no new fluorescence emission peaks (Figure 8) which can be attributed to an ortho photo-Fries rearrangement product. In contrast, photolysis at 280 nm (Xenon lamp) of an amorphous polyurethane (DSC, X-ray analysis) formed from MDI and a poly(ethylene glycol) with molecular weight of 600 results in the appearance of new emission with maximum well above 400 nm due to the ortho photo-Fries product (Figure 9). Thus, in the amorphous polyurethane the ortho photo-Fries product is readily formed in contrast to the semi-crystalline polyurethane in which the rearrangement is apparently inhibited by the restrictive nature of the crystalline morphology. Similar photolysis of a semi-crystalline MDI—dodecanediol polyurethane film (cast from DMF, dried 30 min. at 160°C in a vacuum oven) results only in a loss of fluorescence (Figure 10) from the parent polyurethane, i.e., the ortho photo-Fries product cannot form due to restrictions imposed by the crystalline matrix. By raising the temperature of the MDI—dodecanediol film above the melting point (170°C) and then quenching at room temperature, an essentially amorphous film is obtained. Photolysis of this quenched amorphous film results in a decrease in the fluorescence of the parent polyurethane accompanied by an increase in the fluorescence above 400 nm due to the ortho photo-Fries product (Figure 11). Thus, once again it can be concluded that the crystalline content of the polyurethane matrix severely limits the photo-Fries rearrangement process.

Finally, as might be speculated from the results on photo-Fries product formation, increased crystallinity also lowers the formation of crosslinked gel upon photolysis (Figure 12). The annealed polyurethane, of course, has a high crystalline content (DSC, X-ray analysis) and thus restricts the mobility required for crosslinking to take place. This, incidentally, is similar to the effect that restricted chain mobility has on gel formation (see Figure 4) and absorbance increase at 400 nm (see Figure 3) for 2,4-TDI based polyurethanes.

Photolysis of MDI Based Polyurethane Elastomers

In order to extend our investigation to polyurethane elastomers, a polyurethane elastomer was synthesized by the standard two step method (MDI plus poly(ethylene glycol) with molecular weight of 600 followed by addition of butanediol extender) to give a typical

hard-soft polyurethane elastomer. The ratio of components in the elastomer is given below:

$$MDI:BDO:PEG-600 \equiv 2:1:1$$

MDI = methylene 4,4'-diphenyl diisocyante
BDO = butanediol
PEG-600 = poly(ethylene glycol) or $HO-[-CH_2-CH_2-O-]-_{13.2}H$

Photolysis of the resultant polyurethane elastomer film, when cast from DMF solvent and dried in a vaccum oven at $70^{\circ}C$ for 1 hour, yields the ortho photo-Fries product characterized by fluorescence with emission maximum at 420 ± 10 nm (Figure 13). Two systems were employed in an attempt to stabilize the film. Figure 14 shows that the hindered amine light stabilizer (HALS) and the benzotriazole absorber are both effective in decreasing gel formation on photolysis. As in the case of the simple polyurethane (Figure 7), the benzatriazole UV screener is the most effective stabilizer at the concentrations employed. Once again no attempt was made to optimize the concentration of stabilizer to provide maximum protection.

Conclusions

In this paper, fluorescence analysis was used to detect the formation of ortho photo-Fries products produced by photolysis of MDI and 2,4-TDI based polyurethanes. Based on absorbance and gel formation, both chain mobility and polymer crystalline content were found to have significant effect on the photodegradation of the requisite polyurethanes under investigation. Finally both UV screener and hindered amine light stabilizers were found to be somewhat, although certainly not to the degree one would hope, effective in providing light stability to 2,4-TDI and MDI based polyurethanes.

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312

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Table I

Fluorescence spectral data of model carbamate and expected photoproducts

Compound	Emission Maximum
1a	301 ± 5 nm[a]
1b	337 ± 5 nm[b]
1c	405 ± 10 nm[c]
1d	335 ± 5 nm[d]

[a] 280 nm excitation; 5×10^{-3}M in DMF

[b] 280 nm excitation; 2.5×10^{-4}M in DMF

[c] 280 nm excitation; 1×10^{-4}M in DMF

[d] 280 nm excitation; 5×10^{-5}M in DMF
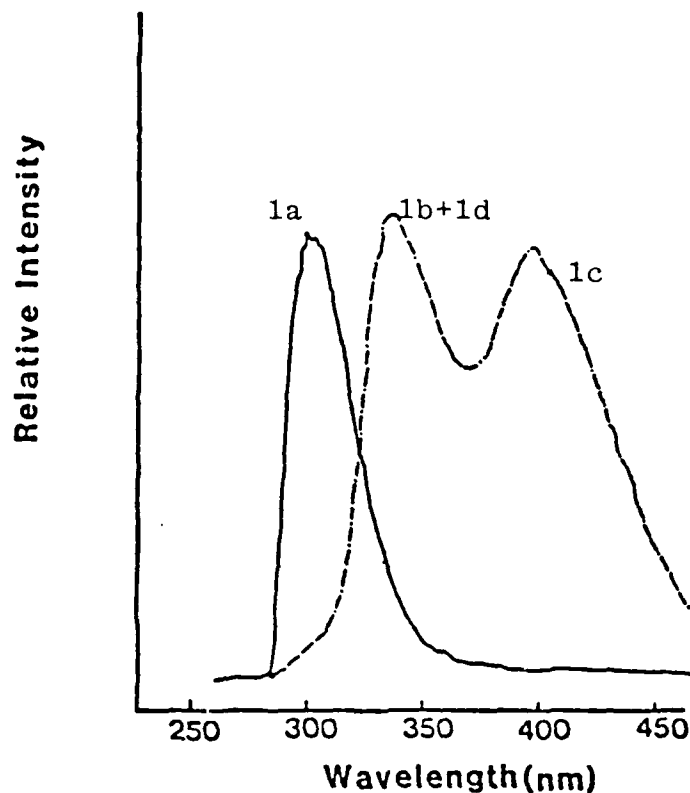
Figure 1. Fluorescence spectral change on photolysis of 2.5 X 10^{-4}M ethyl N-phenylcarbamate in DMF with Rayonet Reactor (300 nm lamps) for 5 hrs. (a) Before pnotolysis _____ (b) After photolysis _ . _ . _.
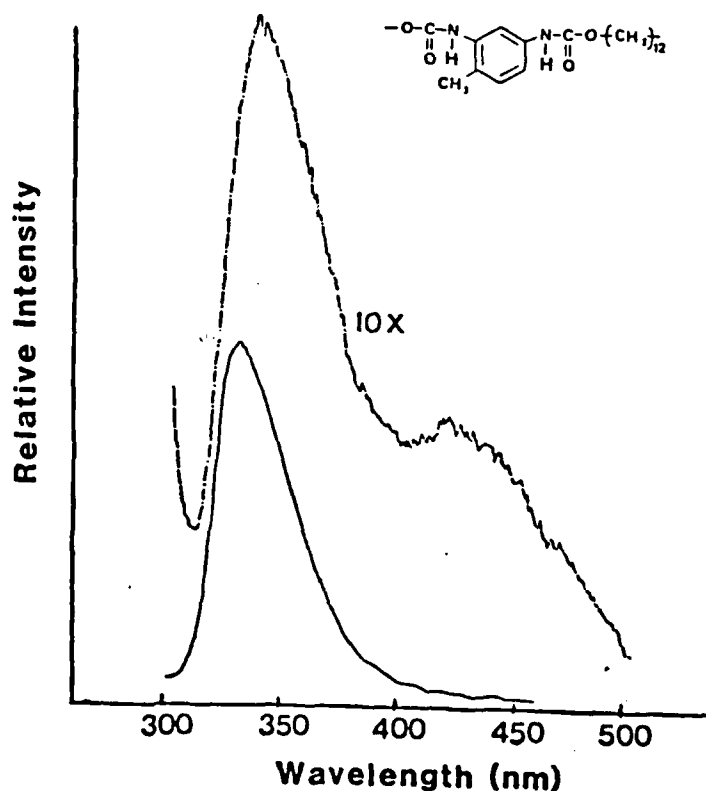
Figure 2. Fluorescence spectral change (λex = 280nm) on photolysis of 2,4-TDI--dodecanediol polyurethane powder with Xenon lamp/ monochromator system at 280nm for 2 hours. (a) Before photolysis _____ (b) After photolysis
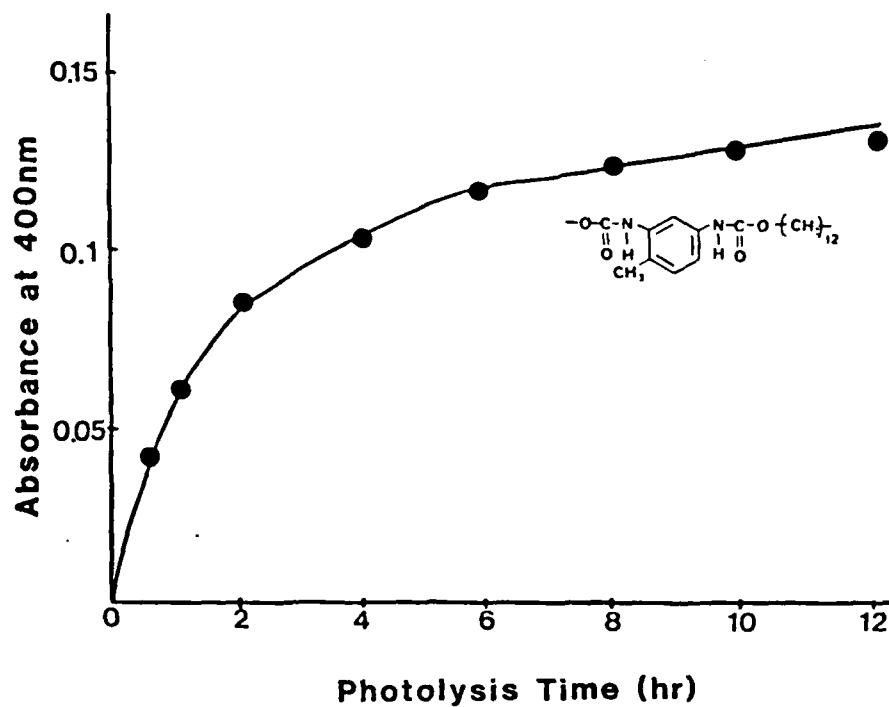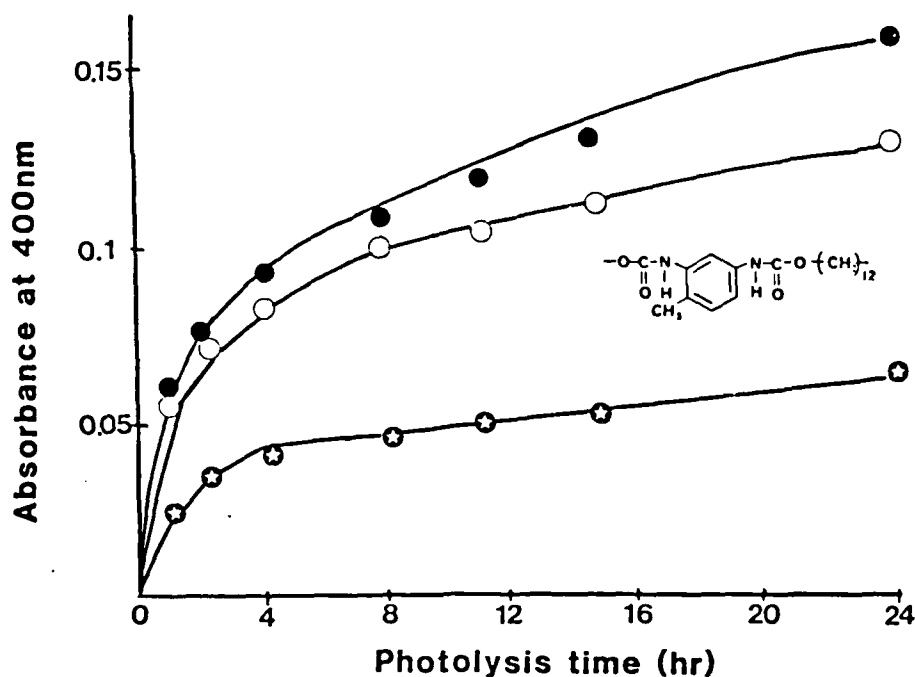
Figure 3. Absorbance change (400 nm) on photolysis of 2,4-TDI--dodecane-
diol polyurethane film with 100 Watt Mercury lamp system.
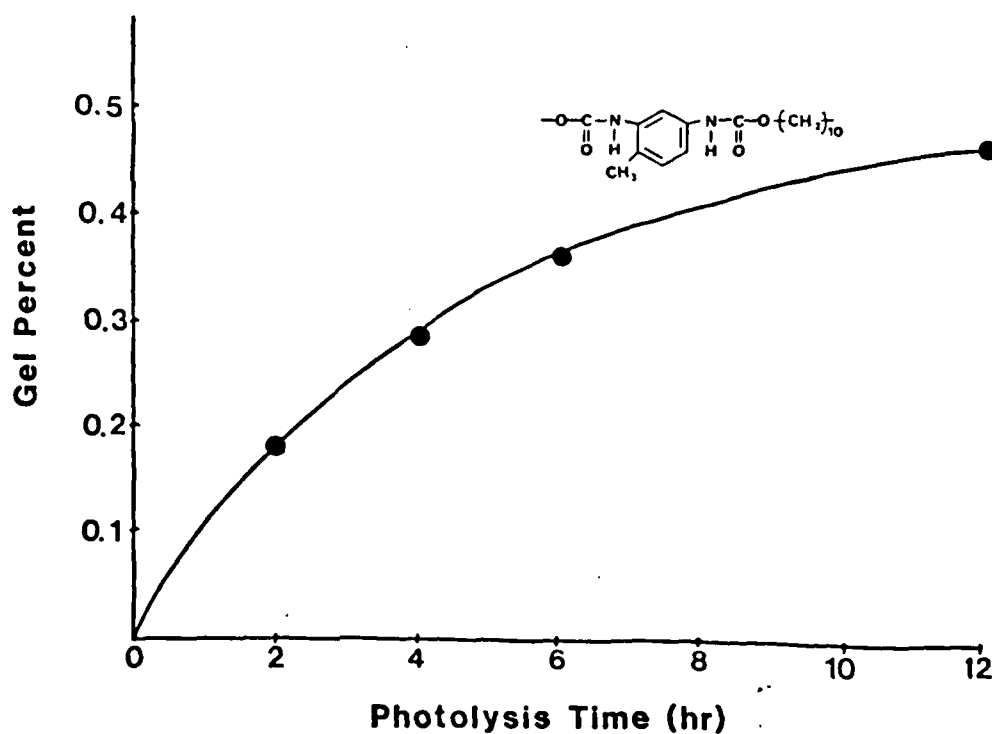
Figure 4. Insoluble gel formation on photolysis of 2,4-TDI--decandeiol
polyurethane film with 100 Watt Mercury lamp system.
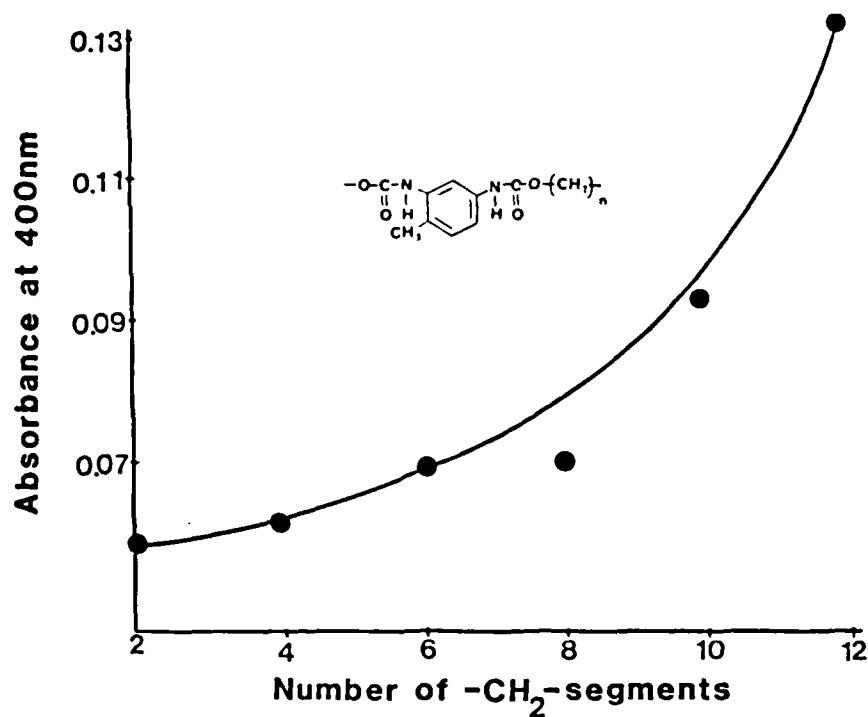
Figure 5. Absorbance changes (400 nm) on photolysis of various 2,4-TDI--aliphatic diol polyurethane films for 2 hours with 100 Watt Mercury lamp system.
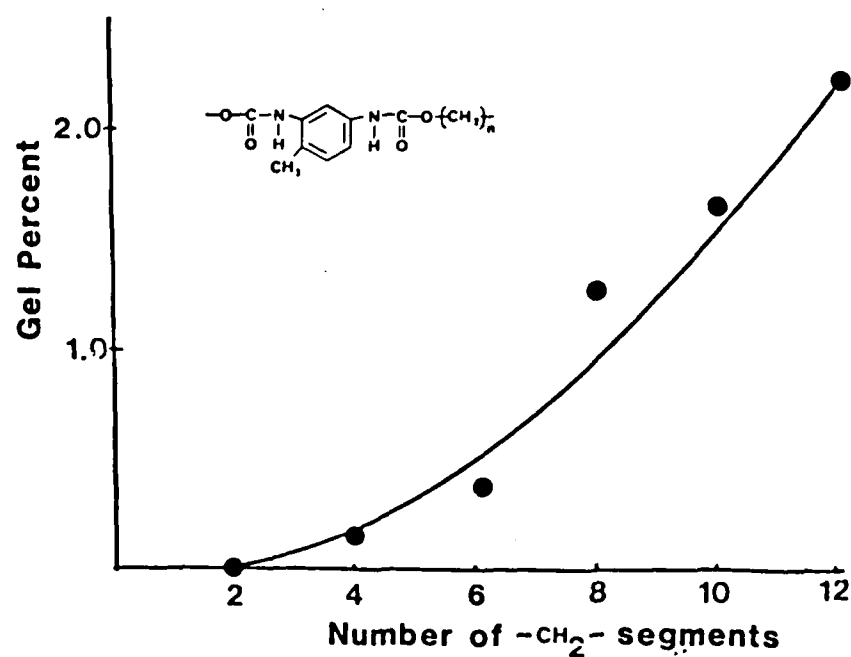
Figure 6. Insoluble gel formation on photolysis of 2,4-TDI--aliphatic diol polyurethane films for 2 hours with 100 Watt Mercury lamp system.

Figure 7.   Absorbance changes (400 nm) on photolysis of 2,4-TDI--
            dodecanediol polyurethane films with 100 Watt Mercury
            lamp system. (a) No added stabilizer ● ● ● (b) 4 wt%
            hindered amine   o o o o o   (c) 4 wt% substituted
            benzotrizole ☉ ☉ ☉ .

Figure 8.   Fluorescence spectral change (λex = 280nm) on photolysis of
            semi-crystalline MDI--diethyleneglycol polyurethane powder
            with Xenon lamp/monochromator system at 280nm for 20 minutes.
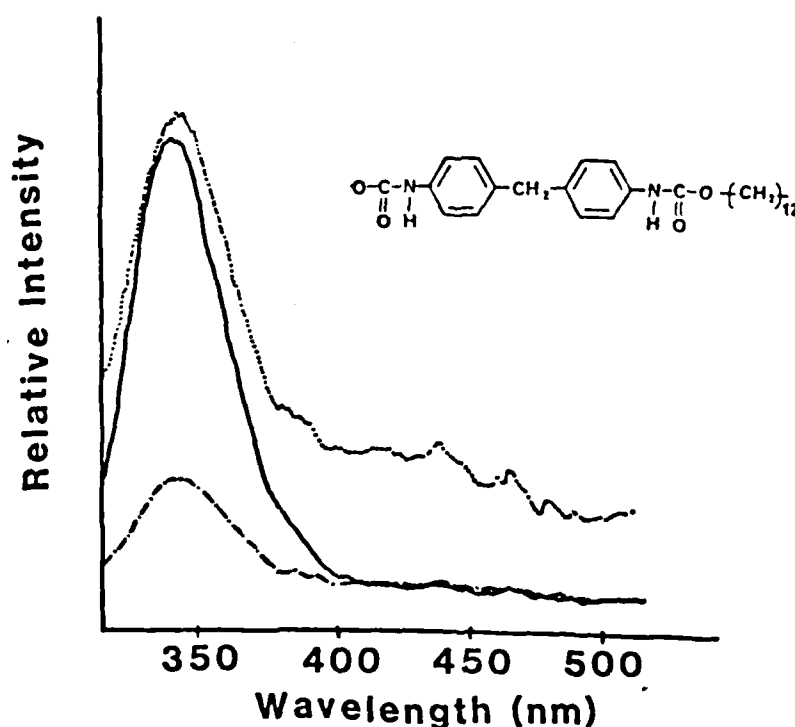   (a) Before photolysis _____ (b) After photolysis
            — . — . — .
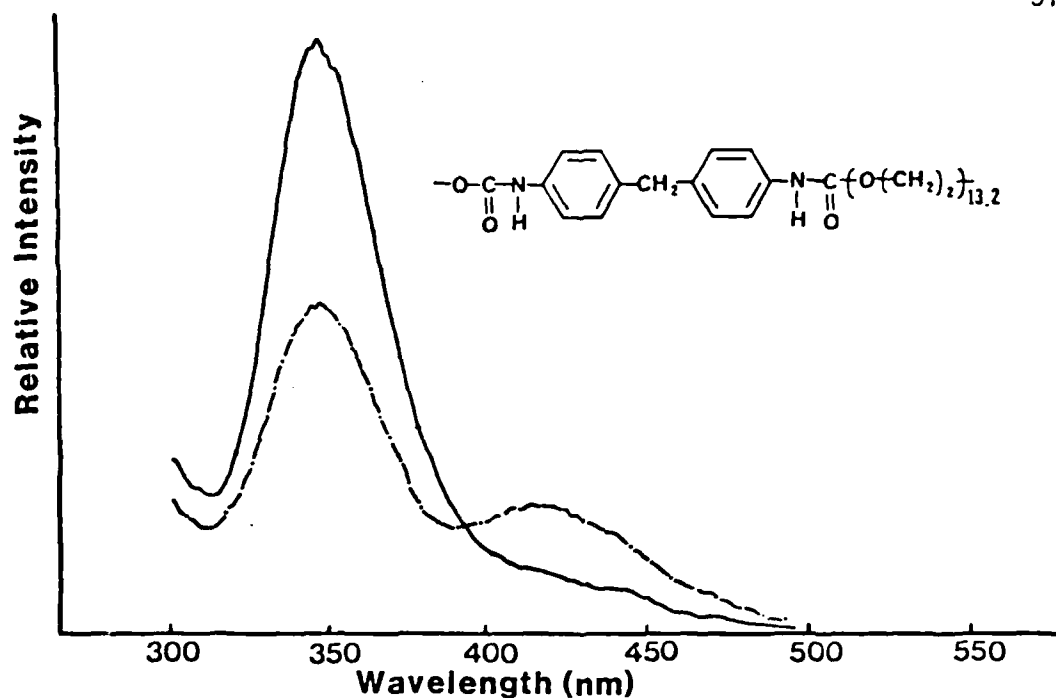
Figure 9.   Fluorescence spectral change (λex = 280 nm) or photolysis of amorphous MDI -- diethyleneglycol polyurethane powder with Xenon lamp/monochromator system at 280 nm for 20 minutes.
(a) Before photolysis _____ (b) After photolysis _ . _ .

Figure 10.   Fluorescence spectral change (λex = 280nm) on photolysis of annealed semi-crystalline MDI--dodecanediol polyurethane film with Xenon lamp/monochromator system at 280nm for 25 minutes.
(a) Before photolysis _____ (b) After photolysis (times 1)___ . ___ . ___ .   (c) After photolysis (times~ 10) . . . .
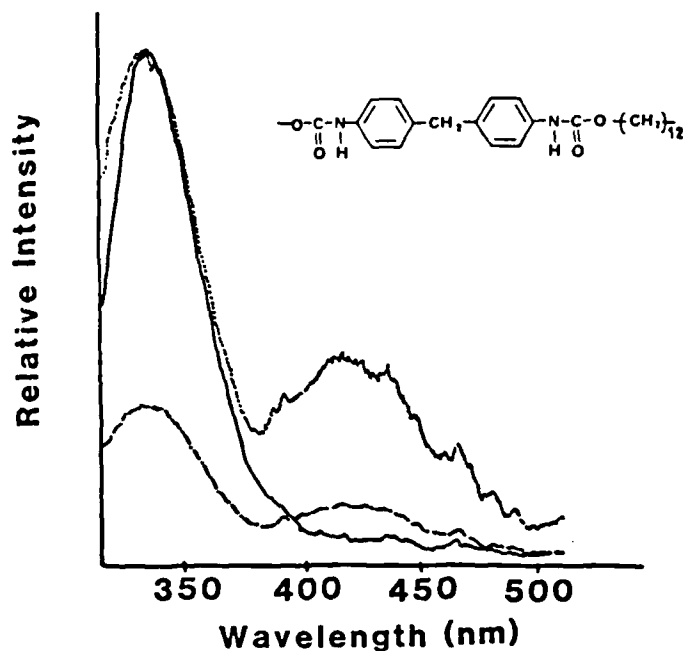
Figure 11. Fluorescence spectral change ($\lambda ex = 280nm$) on photolysis
of thermally quenched amorphous MDI--dodecanediol poly-
urethane film with Xenon lamp/monochromator system at
280nm for 20 minutes. (a) Before photolysis _____
(b) After photolysis (times 1) __ . __ . __ .
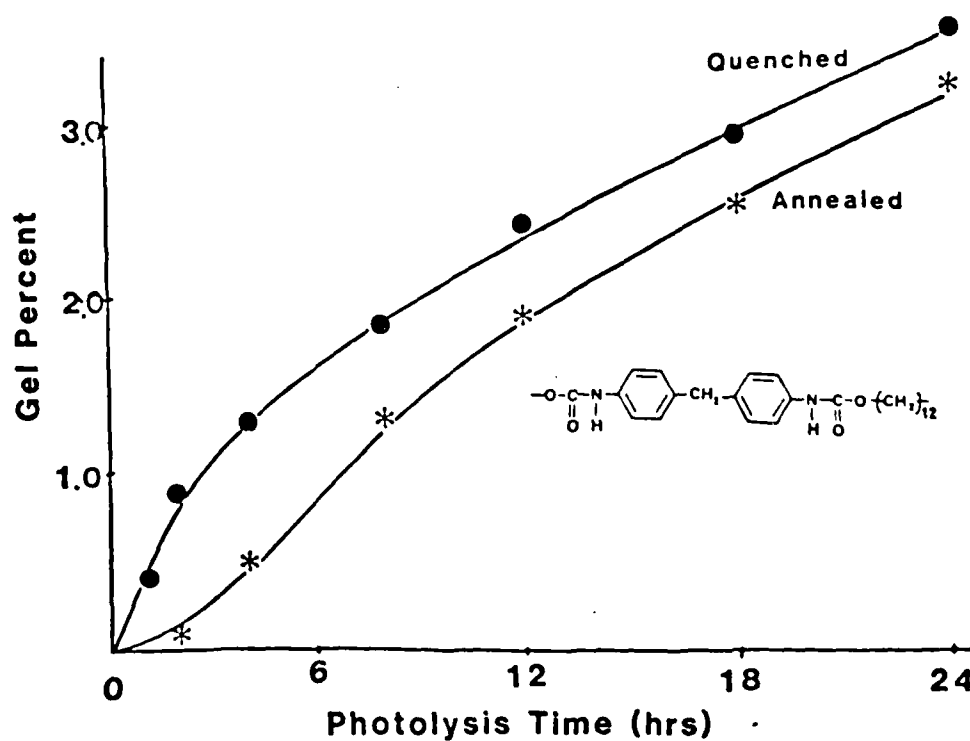(c) After photolysis (times~10) . : . . . . .

Figure 12. Insoluble gel formation on photolysis of MDI--dodecanediol
polyurethane films with Rayonet Reactor (300nm lamps).
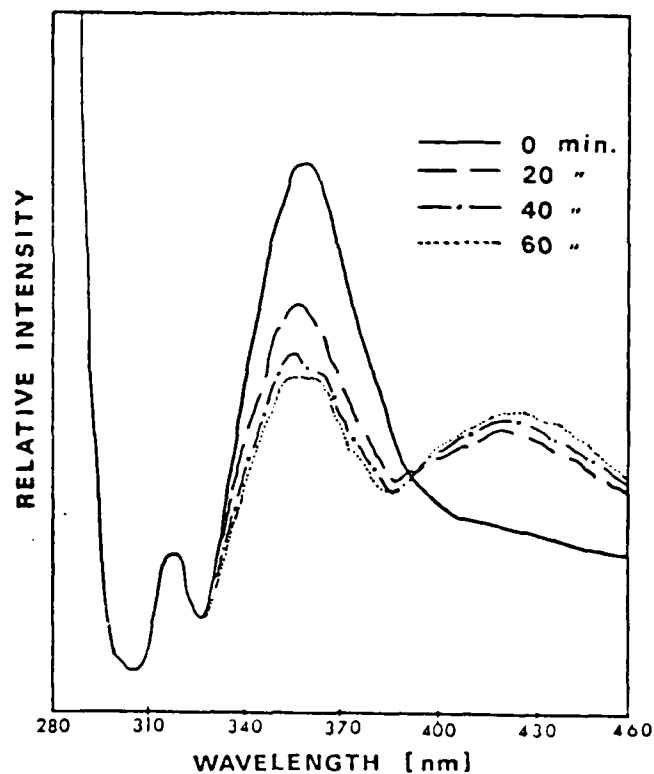(a) Quenched amorphous film ● ● ● ● (b) Annealed semi-
crystalline film * * * * *

Figure 13. Fluorescence spectral change (λex = 280nm) on photolysis
of amorphous MDI--PEG-600 polyurethane film with
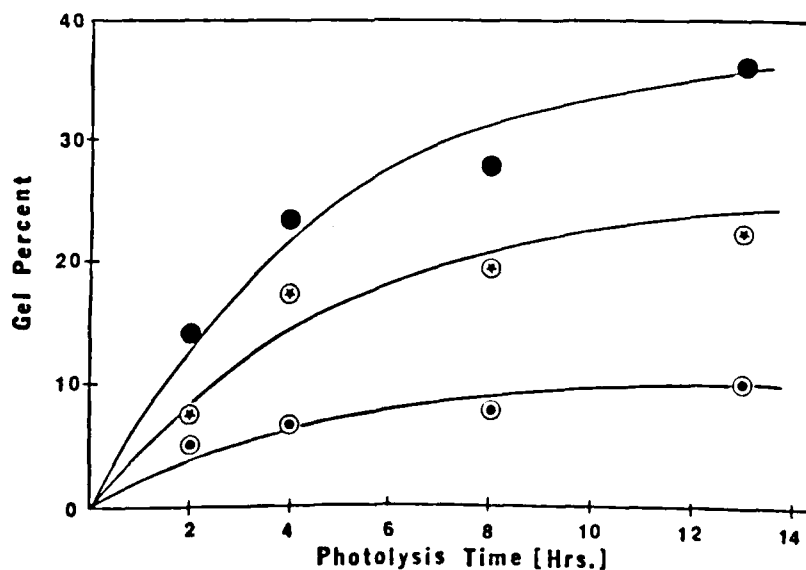Xenon lamp/monochromator system at 285nm.

Figure 14. Insoluble gel formation on photolysis of amorphous MDI--
PEG -600 polyurethane film with Rayonet Reactor (300nm
lamps). (a) No added stabilizer ● ● ● (b) 2.75 wt%
hindered amine ⊛ (c) 4 wt% substituted benzotriazole ◉

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